

Electronic Structure Critical Parameters For the Lithium Isoelectronic Series

Pablo Serra,^{1,2} Juan Pablo Neirotti,¹ and Sabre Kais¹

¹*Department of Chemistry, Purdue University, West Lafayette, Indiana 47907*

²*Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina*

(Received 4 March 1998)

The finite-size scaling method is used to calculate the critical parameters for the lithium isoelectronic series. The critical nuclear charge, which is the minimum charge necessary to bind three electrons, for the ground state was found to be $Z_c \approx 2$. Results show that the analytical behavior of the energy as a function of the nuclear charge for lithium is completely different from that of helium. Analogy with standard phase transitions show that for helium, the transition from a bound state to a continuum is “first order,” while lithium exhibits a “second order phase transition.” [S0031-9007(98)06405-9]

PACS numbers: 31.15.-p, 05.70.Jk

The study of the critical parameters of a quantum Hamiltonian and quantum phase transitions have attracted much interest in recent years [1]. These transitions take place at the absolute zero of temperature, where phase transition means that the quantum ground state of the system changes in some fundamental way as some microscopic parameters change in the Hamiltonian. In atomic and molecular physics, it has been suggested that there are possible analogies between critical phenomena and singularities of the energy [2–4]. Analogies between symmetry breaking of electronic structure configurations and standard phase transitions have been established for many electron atoms and simple molecular systems by studying the corresponding large dimension limit Hamiltonian [5,6].

Recently, we presented the finite-size scaling (FSS) method to calculate the critical parameters for electronic structure [7,8]. In statistical mechanics, the FSS method provides a way to extrapolate information obtained from a finite system to the thermodynamic limit [9,10]. In our applications, the finite size corresponds to the number of elements in a complete basis set used to expand the exact eigenfunction of a given Hamiltonian. In the FSS method we assumed that the two lowest eigenvalues of the quantum Hamiltonian could be taken as the leading eigenvalues of a transfer matrix of a classical pseudosystem. The phenomenological renormalization equation was used to obtain the critical properties of the system. In this approach one has to rely on the analogy to classical statistical mechanics, a more direct finite-size scaling approach without the need to make such an analogy was established by a systematic expansion in a finite (truncated) basis set [11].

The analytical behavior of the energy as a function of parameters for a given system has been the subject of study for many years. In particular, the study of the analytical behavior of the energy as a function of the nuclear charge, Z . Morgan and co-workers [12] have performed a 401-order perturbation calculation to resolve the controversy over the radius of convergence of the $\lambda = 1/Z$ expansion for the ground state energy of the heliumlike ions. Such

high order calculations were necessary to study the asymptotic behavior of the perturbation series and to determine that the radius of convergence, λ^* , is equal to λ_c , the critical value of λ for which the Hamiltonian has a bound state with zero binding energy. Estimating the critical charge, Z_c , is very important in determining if a negative ion is stable or not. The fact that $Z_c = 0.91116 < 1$ for two-electron atoms explains why the H^- is a stable negative ion. Currently there is not a very reliable numerical estimate of the critical nuclear charge nor the radius of convergence of the $1/Z$ expansion for many electron atoms. Although there are well established inequalities based on combinations of mathematical theorems [13] and experimental results, there is not much reliable numerical evidence for testing these inequalities [12]. Accurate and direct estimates of the critical nuclear charges for many electron atoms are the main driving force for introducing new methods, such as the finite-size scaling method, to study the electronic structure critical parameters.

In this Letter we present the first report of an accurate estimate of the critical nuclear charge for three-electron atoms. Using the finite-size scaling method, study of the analytical behavior of the energy near the critical point shows that the open shell system, such as the lithiumlike atoms, is completely different from that of a closed shell system, such as the heliumlike atoms. The transition in the closed shell systems from a bound state to a continuum resemble a “first-order phase transition” while for the open shell system, the transition of the valence electron to the continuum is a “continuous phase transition.”

We may now consider the scaled Hamiltonian of the lithiumlike atoms, which can be written as

$$\mathcal{H}(\lambda) = \sum_{i=1}^3 \left[-\frac{1}{2} \nabla_i^2 - \frac{1}{r_i} \right] + \lambda \sum_{i<j=1}^3 \frac{1}{r_{ij}}, \quad (1)$$

where r_{ij} are the interelectron distances, and λ is the inverse of the nuclear charge.

As a basis function for this procedure we used the Hylleraas-type functions [14] as presented by Yan and Drake [15]

$$\Psi_{ijklmn}(\vec{x}_1, \vec{x}_2, \vec{x}_3) = C \mathcal{A}(r_1^i r_2^j r_3^k r_{12}^l r_{23}^m r_{31}^n \times e^{-\alpha(r_1+r_2)} e^{-\beta r_3} \chi_1), \quad (2)$$

where α and β are fixed parameters, χ_1 is the spin function with spin angular momentum 1/2

$$\chi_1 = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3), \quad (3)$$

C is a normalization constant, and \mathcal{A} is the usual three-particle antisymmetrizer operator [15].

We took $\alpha = 0.9$ and $\beta = 0.1$ in order to obtain accurate results near the critical charge $Z \approx 2$. Note that this choice of the parameters is not the best for a lithium atom with charge $Z = 3$ [15].

In order to calculate the matrix elements of the Hamiltonian Eq. (1) we need integrals of the general form

$$I(i, j, k, l, m, n; \alpha, \beta; \gamma) = \int d^3x_1 d^3x_2 d^3x_3 e^{-\alpha r_1} e^{-\beta r_2} \times e^{-\gamma r_3} r_1^i r_2^j r_3^k r_{12}^l r_{23}^m r_{31}^n. \quad (4)$$

For the numerical evaluation of these integrals, we used an efficient algorithm recently developed by Drake and Yan [16]. All calculations were performed in quadruple precision on an IBM RISC/6000 580. The finite order of the basis set is allowed to be $i + j + k + l + m + n \leq N$. The maximum value of N was taken to be $N = 8$, which gives a 1589×1589 Hamiltonian matrix.

In order to obtain the value of λ_c from studying the eigenvalues of a finite-size Hamiltonian matrix one has to define a sequence of pseudocritical parameters, $\lambda^{(N)}$. Although there is no unique recipe to define such a sequence, in this Letter we used two methods: (i) the first order method (FOM), which can be applied if the threshold energy is known [7,17]. In this method one defines $\lambda^{(N)}$ as the value in which the ground state energy in the N th-order approximation, $E_0^{(N)}(\lambda)$, is equal to the threshold energy E_T ,

$$E_0^{(N)}(\lambda^{(N)}) = E_T(\lambda^{(N)}), \quad (5)$$

and (ii) the phenomenological renormalization (PR) [18] method, where the sequence of the pseudocritical values of λ can be calculated by knowing the first and the second lowest eigenvalues of the \mathcal{H} matrix for two different orders, N and N' . The critical λ_c can be obtained by searching for the fixed point of the phenomenological renormalization equation for a finite-size system with $N' = N - 1$,

$$\frac{\xi_N(\lambda^{(N)})}{N} = \frac{\xi_{N-1}(\lambda^{(N)})}{N-1}, \quad (6)$$

where the correlation length of the classical pseudosystem is defined as

$$\xi_N(\lambda) = -\frac{1}{\log[E_1^{(N)}(\lambda)/E_0^{(N)}(\lambda)]}, \quad (7)$$

and $E_0^{(N)}(\lambda)$ and $E_1^{(N)}(\lambda)$ are, respectively, the ground state and the first excited eigenvalues of a sector of given symmetry of the \mathcal{H} matrix.

In order to obtain the extrapolated value of the sequences $\lambda^{(N)}$ for lithiumlike atoms, we used the general algorithm of Bulirsch and Stoer [19]. The extrapolated value from the PR method was found to be $\lambda_c = 0.48 \pm 0.03$ while the FOM method gives $\lambda_c = 0.497 \pm 0.008$. The results of the pseudocritical inverse charge, $\lambda^{(N)}$, as a function of $1/N$, for $N = 3, 4, \dots, 8$ are shown in Fig. 1. In the neighborhood of the critical charge, the ionization energy for lithiumlike atoms, $I = E_{Li} - E_{He}$, goes smoothly to zero as a function of λ as shown in Fig. 2. This behavior is different from that of our previous results [7,8] for the heliumlike atoms where the ionization energy bends sharply to zero at the helium critical $\lambda_c^{(He)} \approx 1.0976$. The different behavior of the energy as a function of the Hamiltonian parameter, λ , suggests, an analogy with standard phase transitions in statistical mechanics, that the transition from a ground bound state to a continuum in the heliumlike atoms resemble first order phase transitions, while for lithiumlike atoms, the transition is continuous. To investigate this analogy we examined the first and second derivatives of the ionization energy as a function of λ .

In virtue of the behavior of the energy curves, we expect the first derivative of the ionization energy with respect to λ to develop a steplike discontinuity at $\lambda_c^{(He)}$ for the heliumlike atoms [7,8] but will remain continuous for the lithiumlike atoms. Figure 3 shows the first derivative is continuous for lithiumlike atoms as a function of λ .

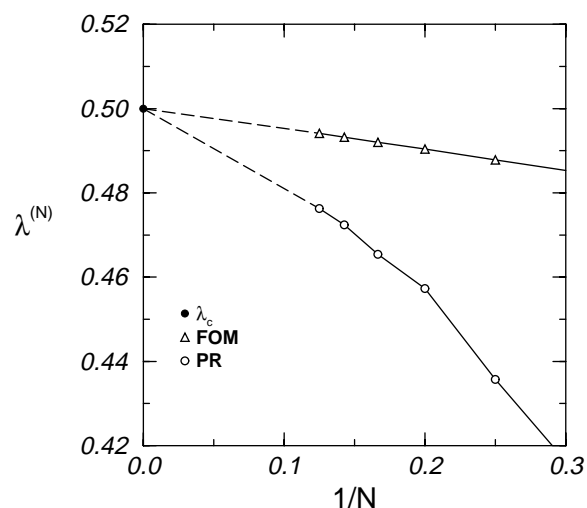


FIG. 1. $\lambda^{(N)}$ for three-electron atoms as a function of the inverse of the system order N . The results are from first order method (FOM) and the phenomenological renormalization (PR).

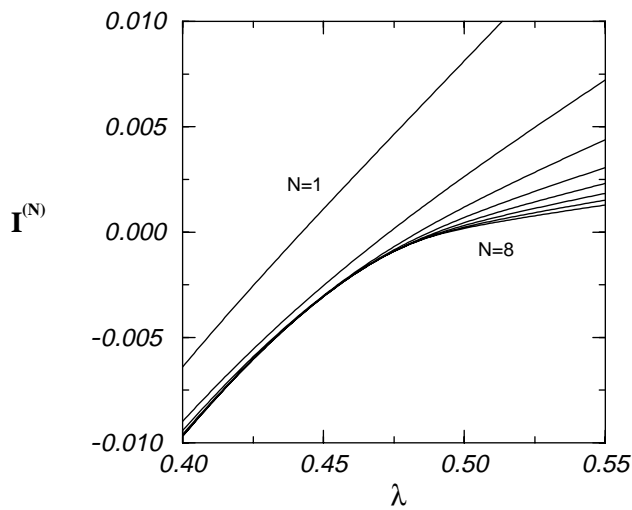


FIG. 2. Ionization energy, $I^{(N)}$, for three-electron atoms as a function of λ for $N = 1, 2, \dots, 8$ ($N = 1$ means five basis functions were used in the calculations and $N = 8$ means 1589 basis functions).

As expected, the second derivative will develop a sharp delta functionlike behavior as N is getting larger for the heliumlike atoms [7,8], but it is much broader for the lithiumlike atoms as shown in Fig. 4.

In a previous study, we showed that for the heliumlike atoms the critical exponent for the energy, $E \approx (\lambda_c - \lambda)^\alpha$; $\lambda \rightarrow \lambda_c^-$, is equal to 1, $\alpha = 1$ [7,8]. This result was in complete agreement with an earlier theorem of Simon and co-workers [20] which proved that $H(\lambda_c)$ for two electron atoms has a square integrable eigenfunction corresponding to a threshold bound state with zero ionization potential and an energy critical exponent $\alpha = 1$. For three electron atoms, we obtained different results;

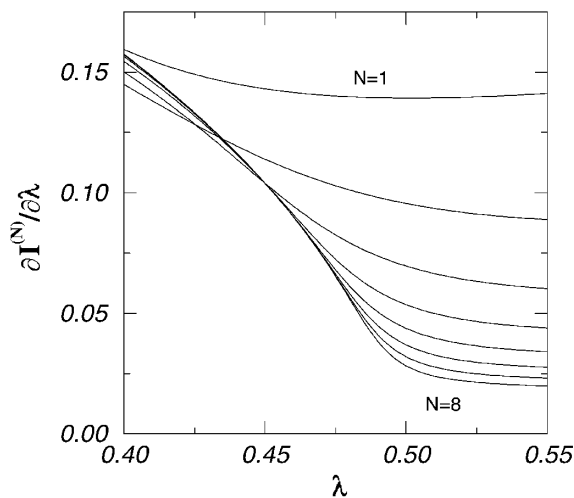


FIG. 3. The first derivative of the ground state ionization energy as a function of λ for the three-electron atoms for $N = 1, 2, \dots, 8$.

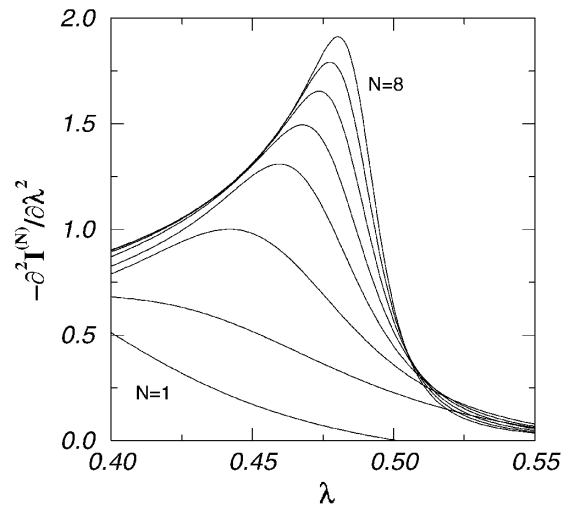


FIG. 4. The second derivative of the ground state ionization energy as a function of λ for the three-electron atoms for $N = 1, 2, \dots, 8$.

the critical exponent was greater than 1. Figure 5 shows the extrapolated value of the numerically fitted exponent as a function of $1/N$ for $N = 1, 2, \dots, 8$. This value was found to be $\alpha \approx 1.64 \pm 0.05$. Contrary to the helium case, where the Hamiltonian has a square integrable eigenfunction at $\lambda^{(\text{He})} = \lambda_c^{(\text{He})}$, the Hamiltonian for lithiumlike atoms does not have a square integrable wave function at the bottom of the continuum.

Finally, the behavior of the correlation length $\xi^{(N)}$, for the associated classical pseudosystem [8] as a function of λ is shown in Fig. 6. In this figure, the behavior of the correlation length is characteristic of a continuous phase transition using the finite-size scaling method, which goes like an inverse power law in $(\lambda - \lambda_c)$.

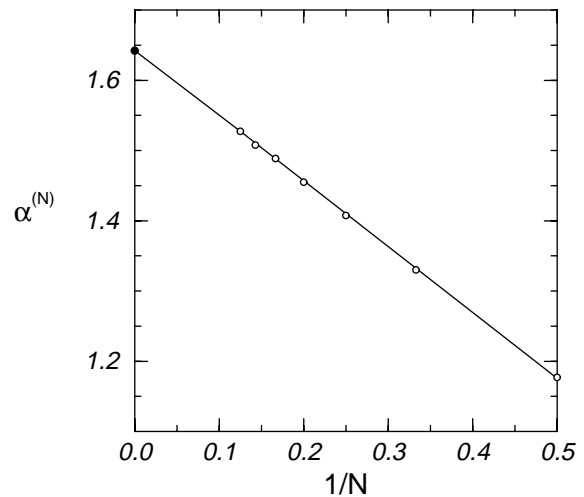


FIG. 5. The exponent, $\alpha^{(N)}$, for the energy of the three-electron atoms as a function of the inverse of the system order N .

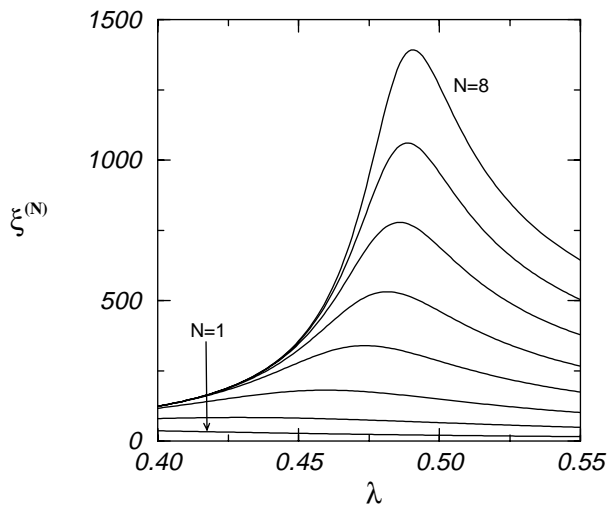


FIG. 6. The correlation length, $\xi^{(N)}$, as a function of λ for the three-electron atoms for $N = 1, 2, \dots, 8$.

In summary, results show that there is a fundamental difference in behavior of the energy as a function of λ for the closed shell heliumlike atoms and the open shell lithiumlike atoms. The transition in the former between a bound state to a continuum has all the characteristics of first-order phase transition while the latter has a continuous phase transition. Although in atomic physics only integer values of the nuclear charge have a physical meaning, this procedure gives a direct method to predict the stability of atomic negative ions by studying an isoelectronic series of like atoms. Results show that while H^- is a stable negative ion, He^- is not stable since the critical charge is at the limit of the He atom. Research is underway to calculate critical charges for other atoms to verify if one can classify atoms in the periodic table according to their type of phase transition and whether or not there are more than two kinds of phase transitions.

We thank Professor G. W. F. Drake and Dr. Zong-Chao Yan for sending us the Fortran code to calculate the general three electron integrals, Eq. (4) in the text. We also acknowledge the financial support of the Office of Naval Research (N00014-97-1-0192). One of us (P.S.)

thanks CONICET and SECYTUNC for partial financial support.

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